Bombardment of solid glycine by 2 keV electrons. Implications for astronomical environments

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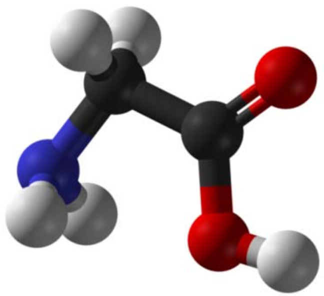
Funding:
CDS2009-00038, FIS2013-48087-C2-1-P
ERC-2013-Syg 610256

ISACC 2015, Madrid, July 20, 2015

Outline

- Introduction
- Electron bombardment of glycine
  - Cross sections and radiolysis yields
  - Irradiation products
- Astronomical implications

Glycine in extraterrestrial environments ?



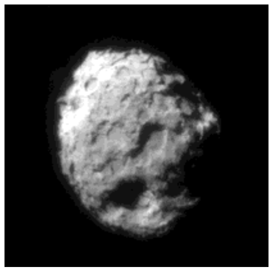
NH_2-CH_2-COOH

- Simplest amino acid
- Prototype for studies of prebiotic molecules in space

Murchinson meteorite

- Detected in carbonaceous condrites together with other amino acids

  O. Botta & J. L. Bada 2002, S. Geo, 23, 411



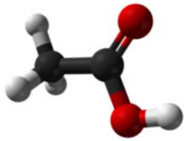
Comet 81P/Wild2

- Detected in one comet ("stardust" mission)

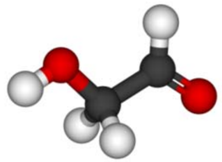
  J. Elsila et al. 2009, M&PS 44, 1323

Glycine in the interstellar medium ?

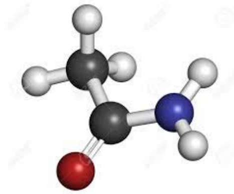
- Complex (> 6 atoms) organic molecules are found in the interstellar medium
  - E Herbst & E. F. van Dishoeck, 2009. ARA&A, 47,427



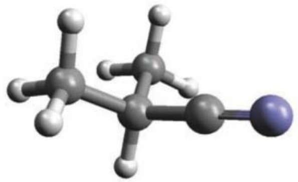
Formic acid



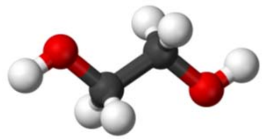
Glycol aldehyde



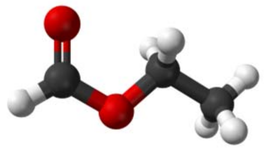
Acetamide



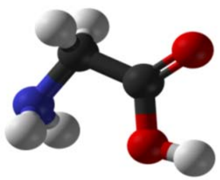
Isopropyl cyanide



Ethylene glycol



Ethyl formate



?

Glycine

- Reported detections of glycine have been questioned and are, as yet, inconclusive
  - L. E. Snyder et al. 2006, ApJ 647,412

Destruction of molecules in space

- Main destruction processes for molecules in space:
  - UV radiation
  - Cosmic rays

- Cosmic rays (CRs): high energy (keV-GeV) particles.
  - Mostly protons, also electrons and other nuclei
  - The interaction of CRs with matter leads to cascades of secondary electrons and to bremsstrahlung photons
  - Most chemical effects are due to secondary electrons with energies < 20 eV
  - The relevant magnitude for chemical damage by CRs is often assumed to be the energy dose recived by a sample **irrespective of the nature of the original CR particle**

Laboratory processing of glycine with energetic particles

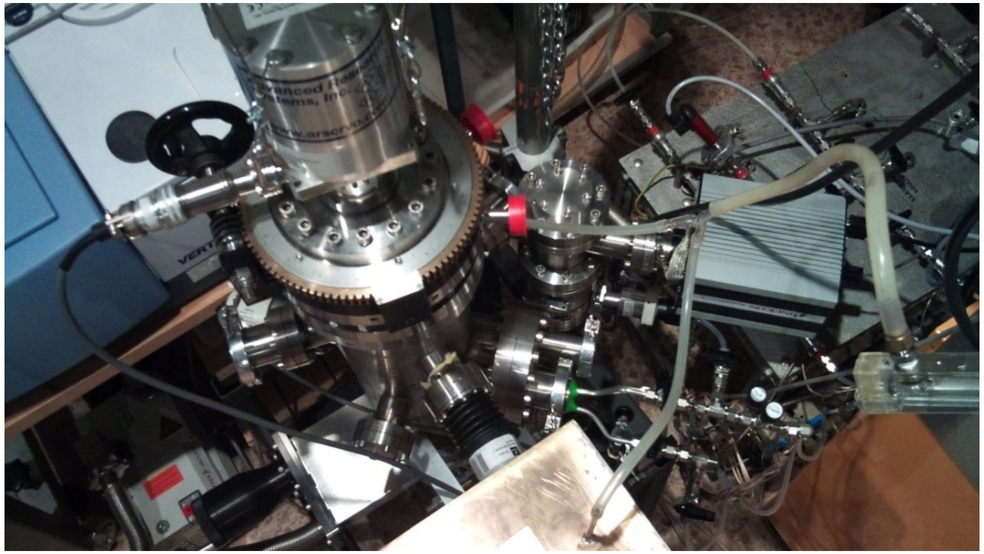
- Bombardment of glycine with 0.8 MeV protons
  - P. A. Gerakines et al. 2012, Icarus, 220, 247
- T: 15-140 K
- Number of glycine molecules destroyed per deposited energy: **(3.3 – 5.8)/100 eV**

- Bombardment of glycine with 2 keV electrons
  - S. Pilling et al. 2014, EPJD, 68, 58
- T: 15 K and 300 K
- Number of glycine molecules destroyed per deposited energy: **(0.15-0.93)/100 eV**

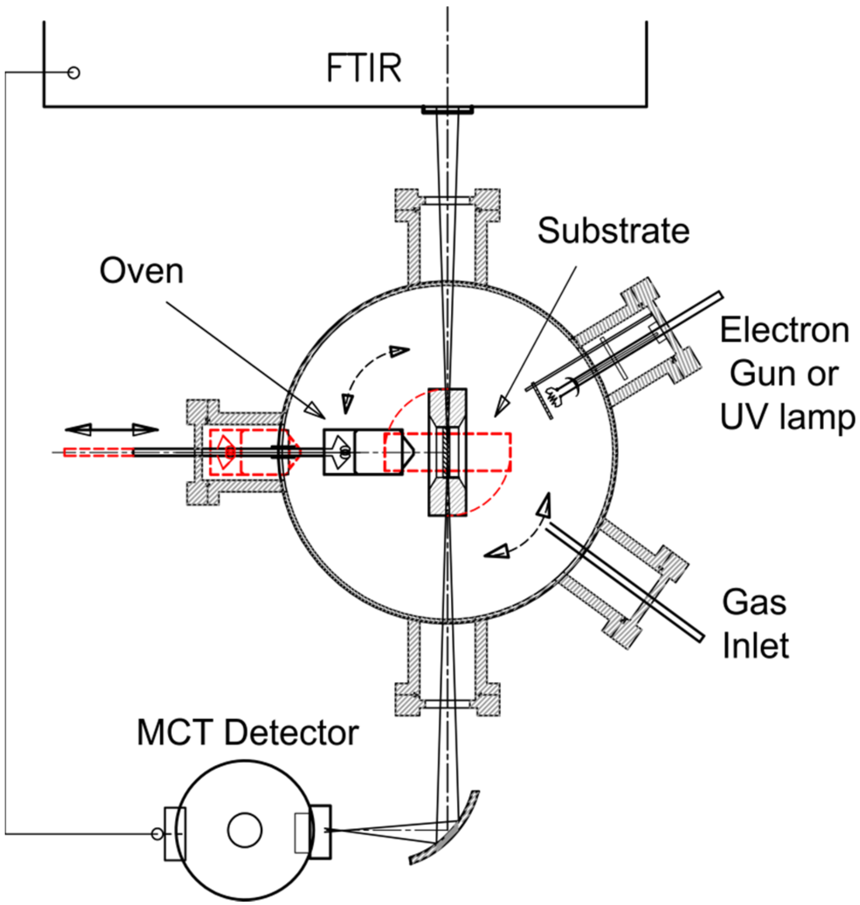
Protons seem to be much more effective for the destruction of glycine (in contrast with previous assumptions)

Experimental set-up

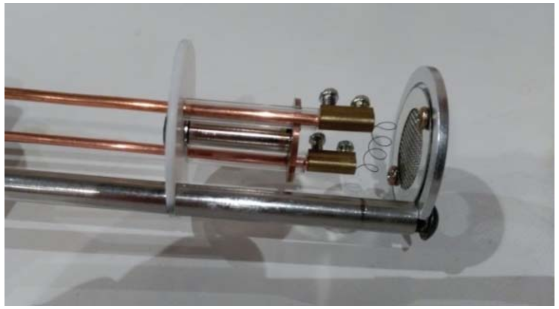
- Vacuum chamber with P_b~ 10^{-8} mbar
- Closed cycle He Cryostat 14-300 K
- Fourier transform infrared (FTIR) spectrometer
- Si substrate; normal incidence transmission



Scheme of the experiment

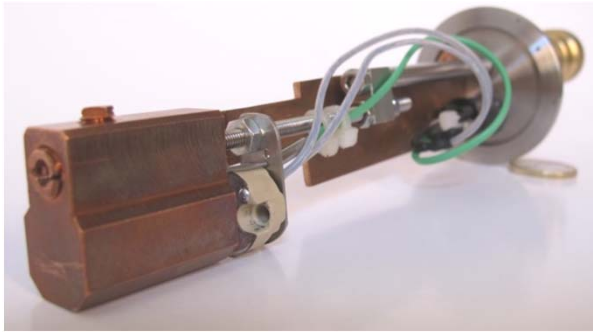


Electron gun



2 keV electrons
8×10^{11} cm^{-2} s^{-1}

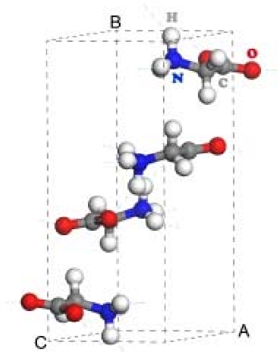
Glycine oven



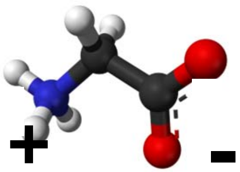
150 ºC

- B. Maté et al. 2014, FD, 168, 267

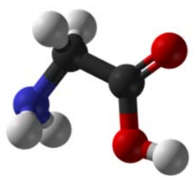
IR spectra of vapor deposited glycine



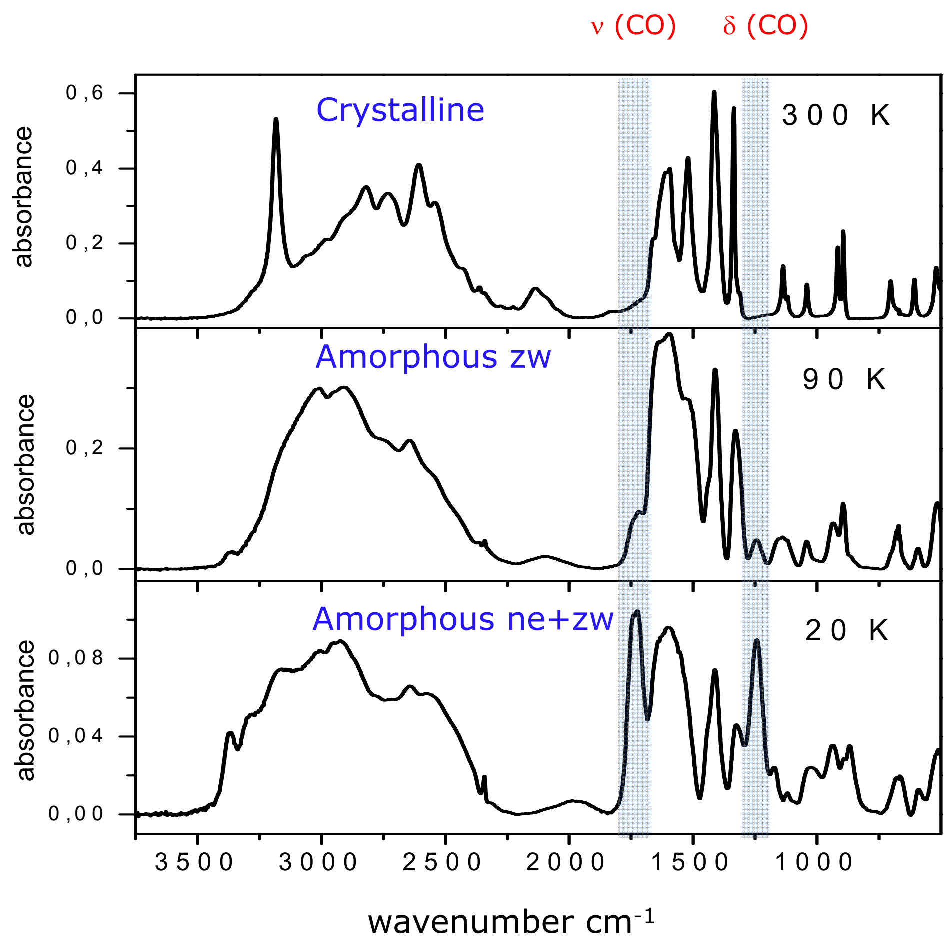
Crystalline



Zwitterionic

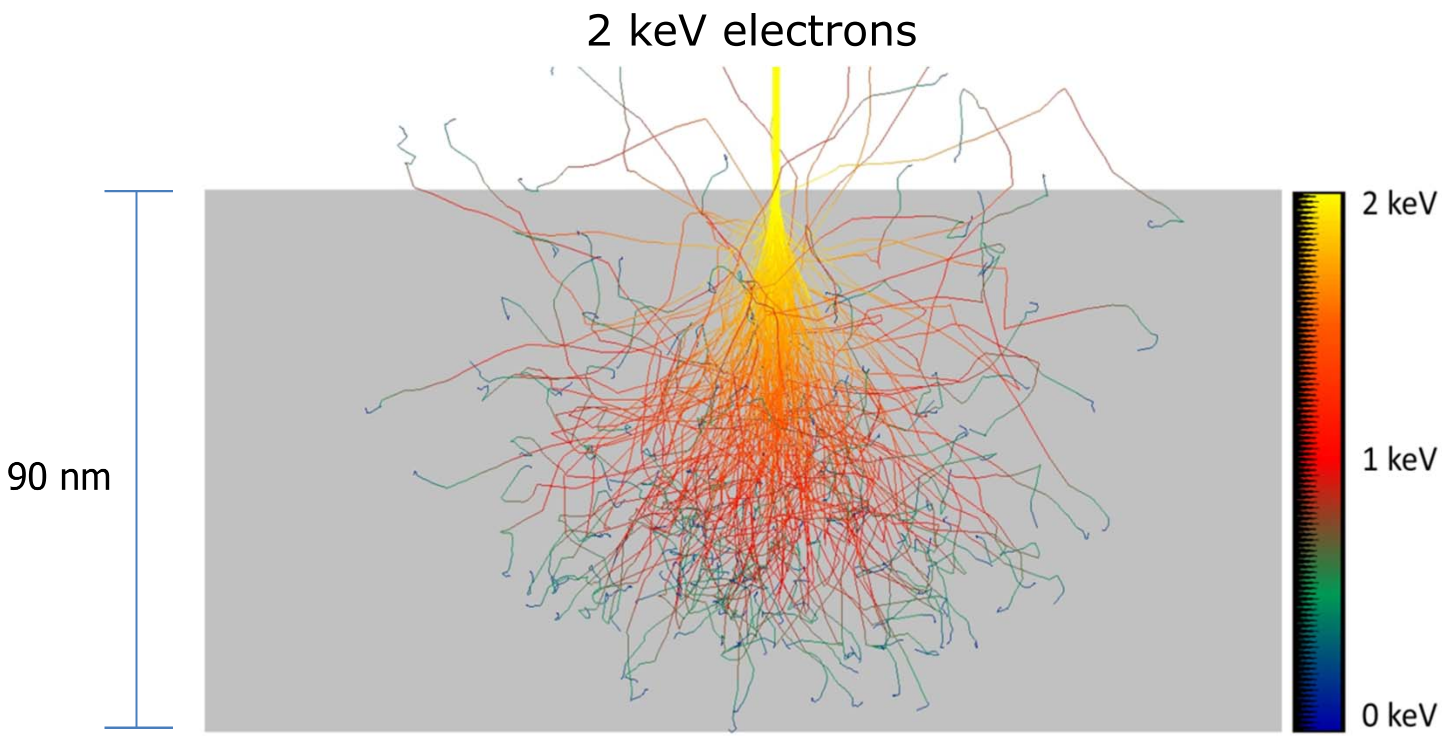


Neutral



Electron penetration depth in glycine

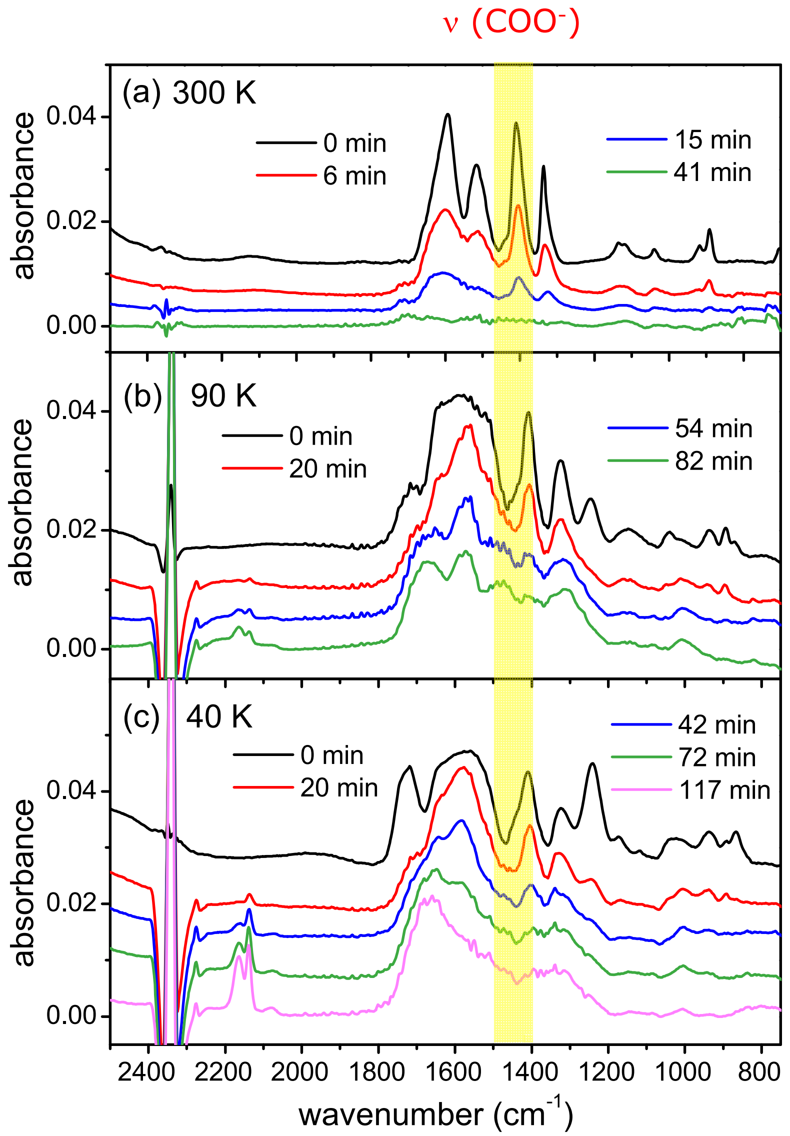
Monte Carlo ("CASINO")* simulation



Linear energy transfer (LET): 22 keV μm^{-1}

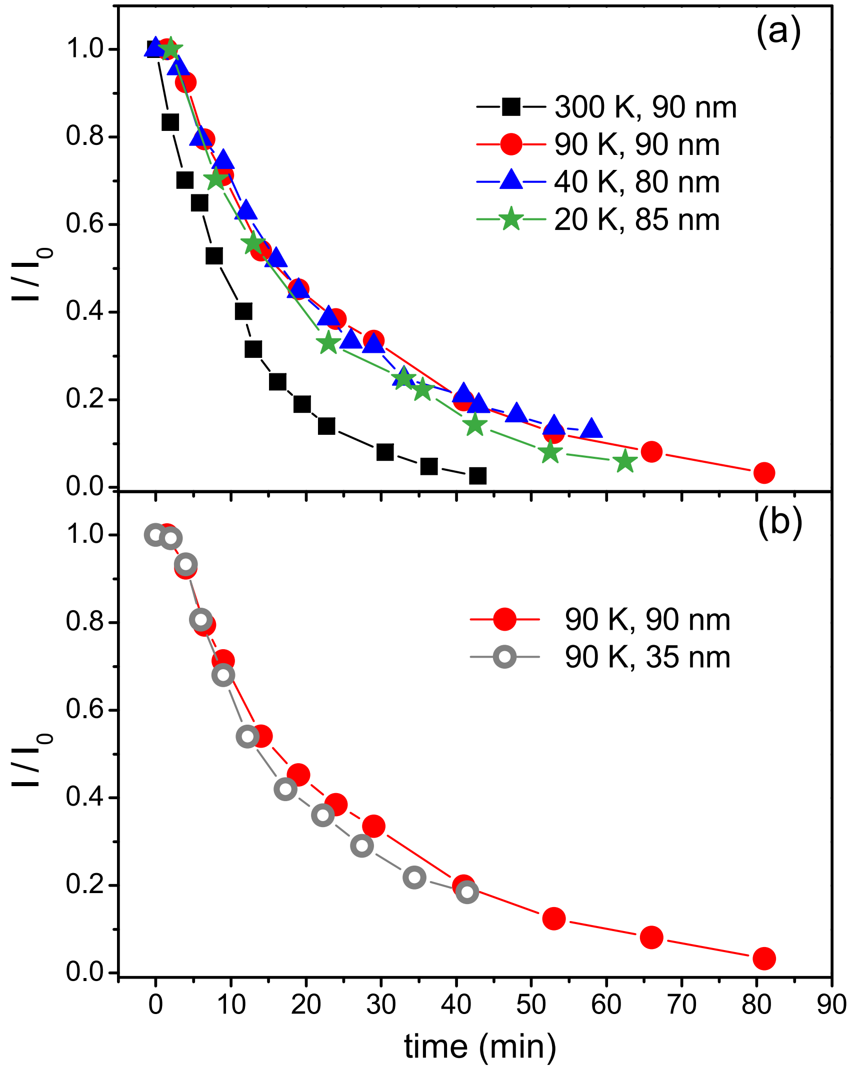
* Monte **CA**rlo **S**Imulation of electro**N** trajectories in s**O**lids
  - D. Drouin et al. 2007, Scanning, 29, 92

Spectral evolution upon electron irradiation



- The decay of the 1400 cm^{-1} band is used to follow the destruction of glycine
- At 300 K nothing is left of the sample → primary radiolysis products are volatile and evaporate
- For temperatures lower than 90 K, irradiation leads to new peaks between 2400 and 2000 cm^{-1} and blurs the peak structure between 1800 and 1200 cm^{-1}, leaving a broad absorption band.
- This broad band is associated with a residue that does not disappear upon heating to 300 K

Decay of the 1400 cm^{-1} band

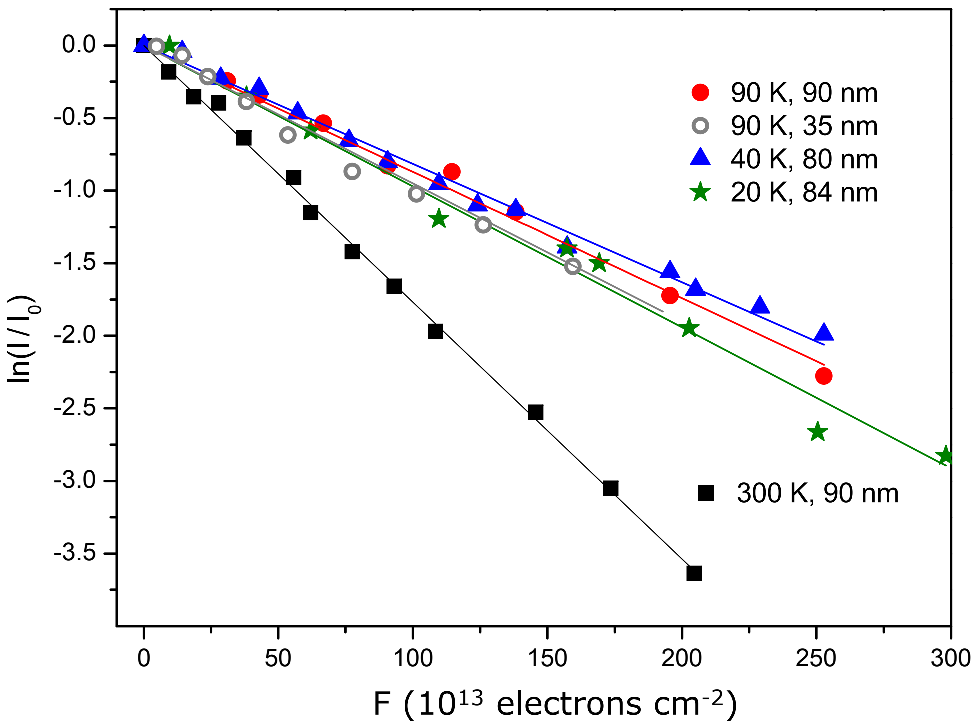


- For T< 90 K the evolution is independent of T
- At 300 K glycine destruction is faster
- The decay is the same for 90 and for 35 nm → the 90 nm sample is wholly irradiated

Kinetics of glycine destruction

- Single forward first order reaction :

$$\ln\left(\frac{[\mathrm{Gly}]}{[\mathrm{Gly}_0]}\right) = -kt$$



$$\ln\left(\frac{I}{I_0}\right) = -\sigma F$$

- B. Maté et al. 2015, ApJ, 806, 151

Destruction cross sections and radiolysis yields

The radiolysis yield (G) is defined as the number of molecules destroyed by 100 eV of absorbed radiation

$$G = 100\frac{N_0\left(1 - e^{-\sigma F}\right)}{\mathrm{LET}\; h\; F}$$

N_0 = initial column density, σ = destruction cross section,
LET = Linear energy transfer, F = electron fluence, h= sample thickness

Glycine sample	σ (10^{-16} cm^2)	G (molecules/100 eV)
300 K, 90 nm	17.6 ± 1	10.2 ± 1
90K, 90 nm	8.7 ± 1	5.1 ± 0.6
90 K, 35 nm	9.5 ± 1	5.5 ± 0.6
40 K, 80 nm	8.2 ± 1	4.8 ± 0.6
20 K, 85 nm	9.7 ± 1	5.6 ± 0.6

The G values corespond to the begining of irradiation, i.e. F $\rightarrow$ 0

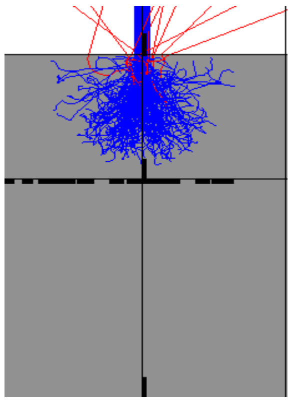
Comparison with previous results:

- S Pilling et al. 2014 EPJD, 68, 58
- α, β- glycine processed with 2 keV electrons

Radiolysis yield G (molec/100eV)					
Pilling et al. 2014				This work	
α-gly, 300 K	**0.18**	β-gly, 300 K	**0.15**	β-gly, 300 K	**10.2 ± 1**
α-gly, 14 K	**0.93**	β-gly 14 K	**0.84**	Amorph, 20K	**5.6 ± 0.6**

Main experimental differences:

- Not always the same polymorphs
- Samples in Pilling et al. thicker (0.8 -4.6 μm)
  → incomplete processing

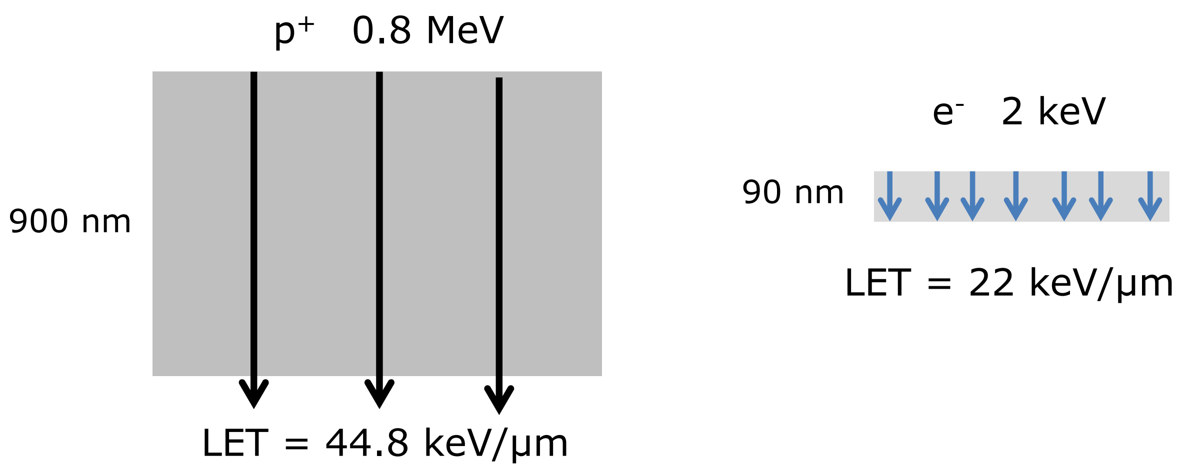


Comparison with previous results:

- P. A. Gerakines et al. 2012 Icarus, 220, 647
- Amorphous glycine processed with 0.8 MeV protons

Radiolisis yield G (molec/100eV)			
Gerakines et al. 2012		This work	
Amorph, 100 K	**3.6 ± 0.5**	Amorph, 90 K	**5.1 ± 0.6**
Amorph, 14 K	**5.8 ± 0.5**	Amorph, 20K	**5.6 ± 0.6**

Scheme of the experiments:



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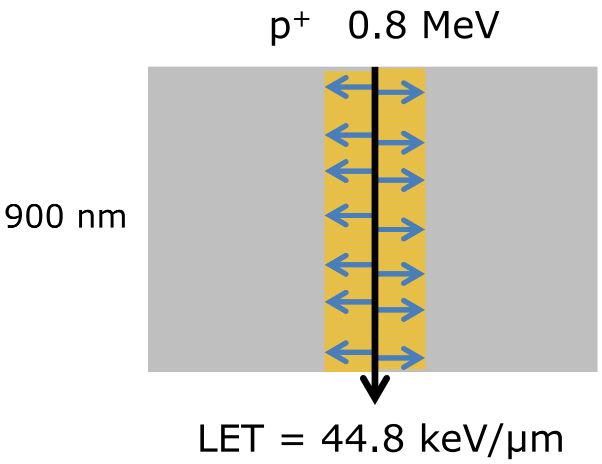

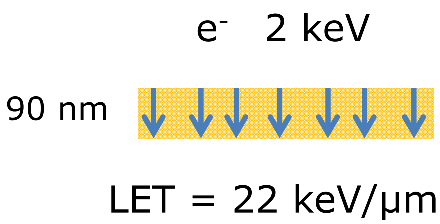

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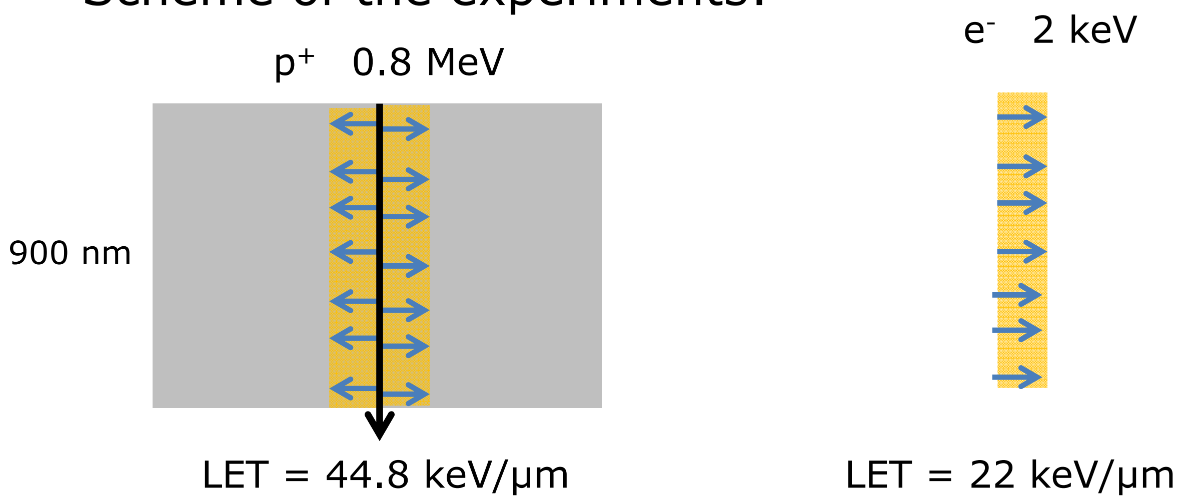
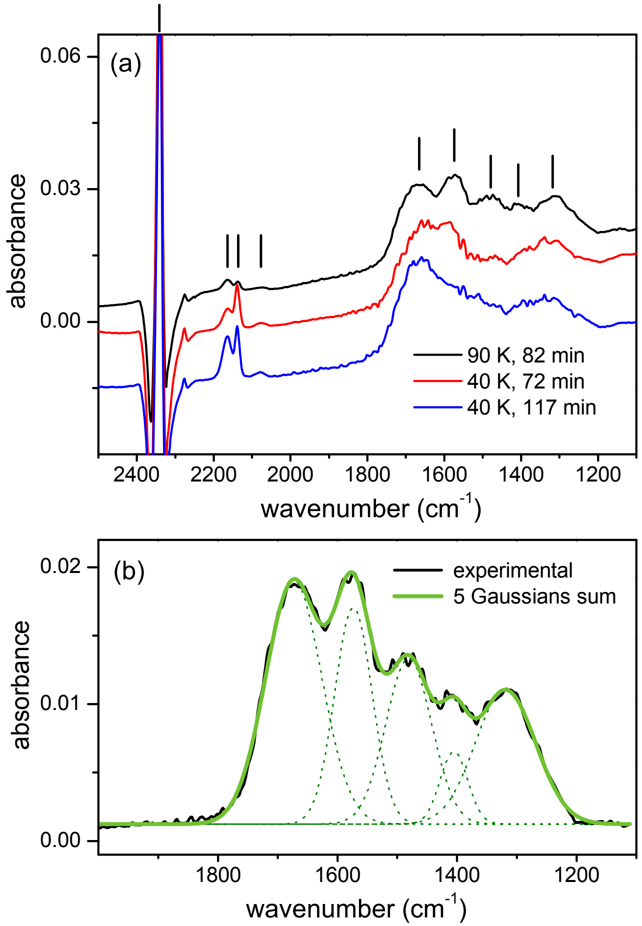


Irradiation products

Spectra of residues

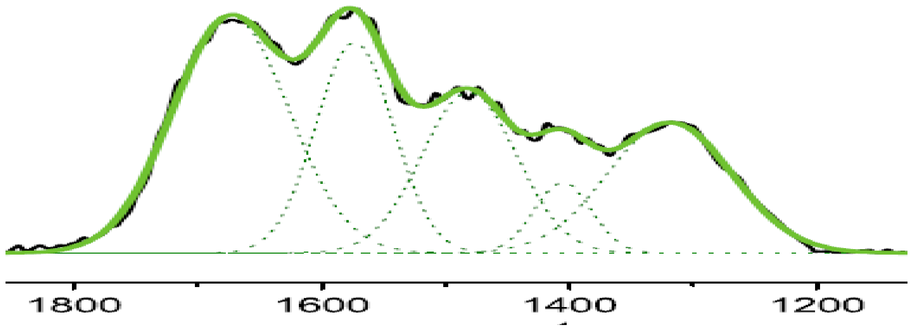


Tentative assignment

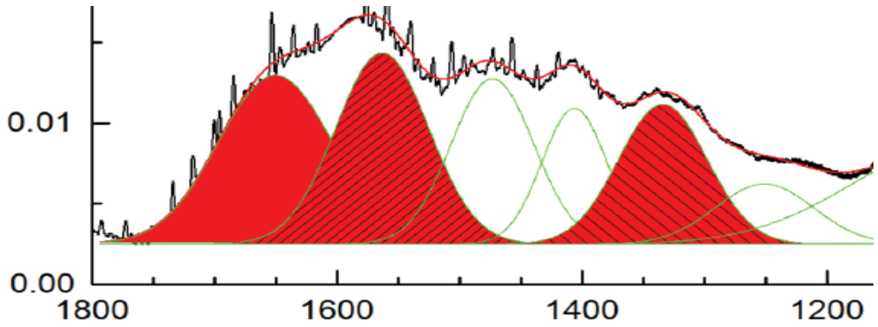
Carrier	Band center, cm^{-1}
CO_2	2340
OCN^-	2164
CO	2136
CN^-	2077
Amide I	1673.3
Amide II	1573.4
Deform., scissor $-CH_3$, $-CH_2$	1480.9
Stretching, $-RCO_2^-$	1405.2
Amide III	1319.0

Comparison with previous work

Amide bands ?



- Electrons, 2 keV
  90K, amorphous
- B. Maté et al.
  2015, ApJ , 806. 151
  (This work)



- $^{58}Ni^{11+}$ ions, 46 MeV
  14 K, α glycine
- W. Portugal et al.
  2014 , MNRAS, 441, 3209

Radiation chemistry of amino acids

- Complex chemistry with multiple reaction pathways
  - E. Sagstuen et al., 2004, Rad. Research, 162, 112

Relevant processes for glycine:

Decarboxylation

$^{+}NH_3CH_2COO^{-} \longrightarrow NH_2CH_3 + CO_2$

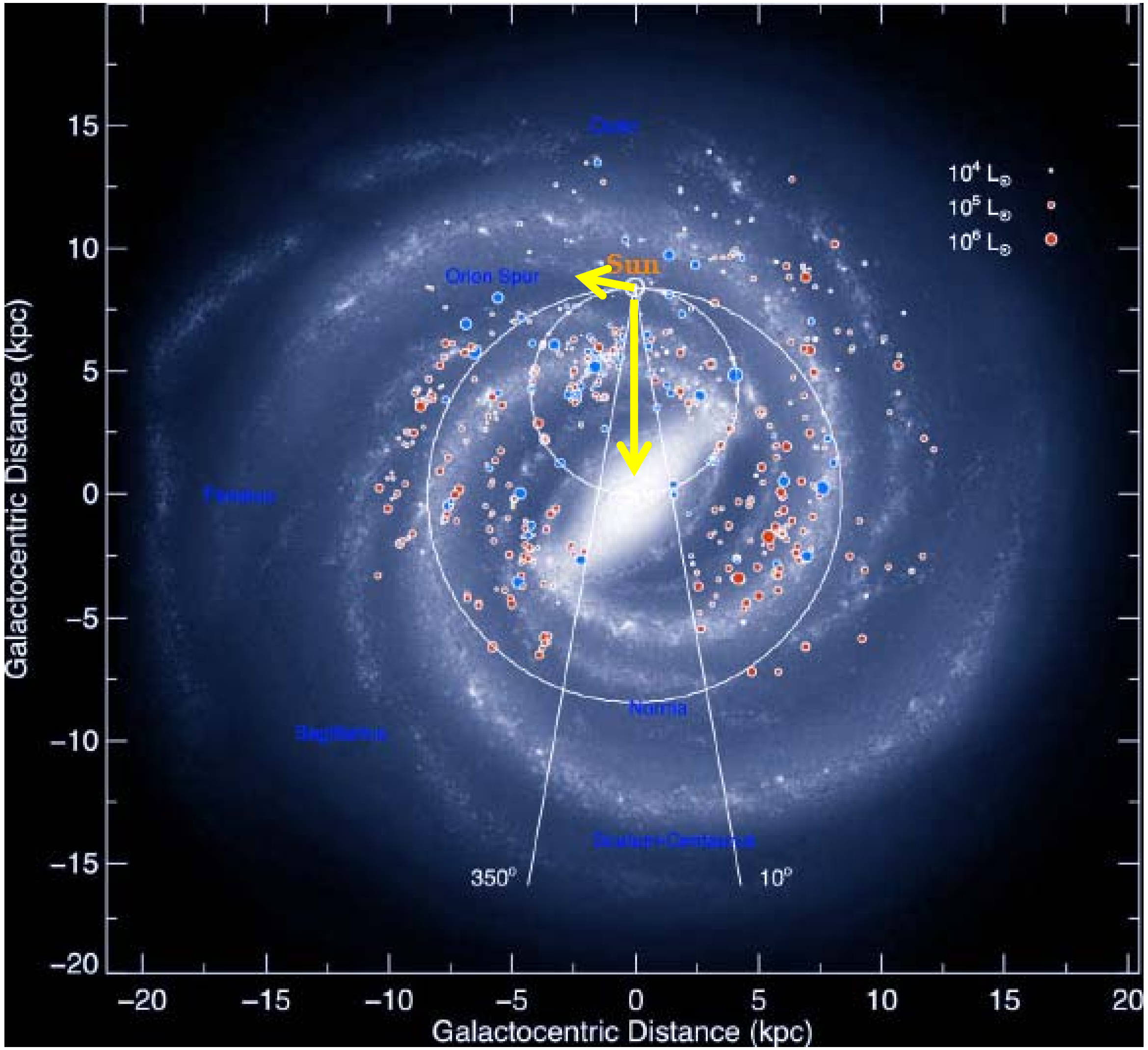
Deamination

$^{+}NH_3CH_2COO^{-} \longrightarrow NH_3 + CH_2COO^{\cdot}$

Formation of peptide bonds

$2\,(^{+}NH_3CH_2COO^{-}) \longrightarrow NH_2\,CH_2CO\text{-}NH\text{-}CH_2COOH + H_2O$

The milky way



1 kpc = 3 x 10^{16} km

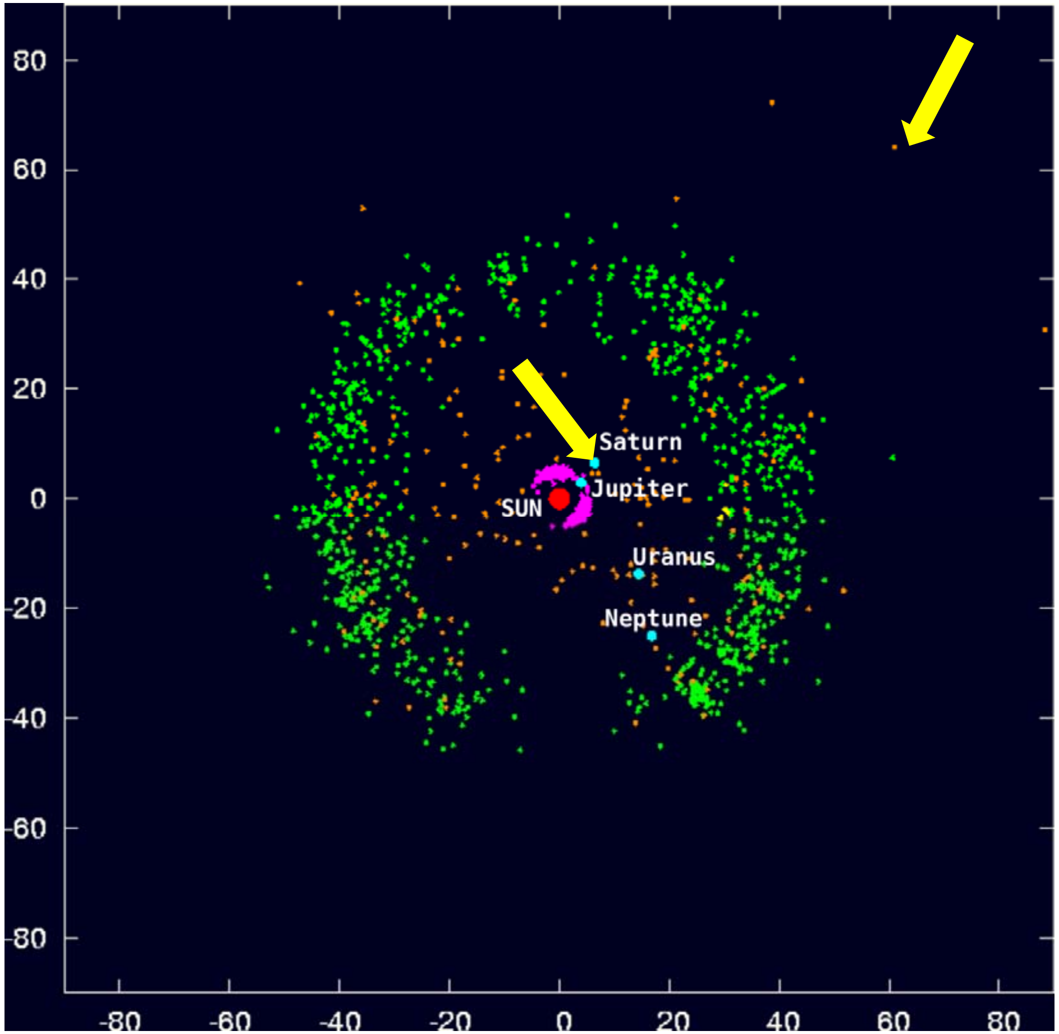
Interstellar medium

				Glycine half-life (yr)		
	Location	T (K)	Radiation dose rate[1] (eV yr^{-1})	This work 2 keV electrons	Gerakines et al. 0,8 MeV protons	Pilling et al. 2 keV electrons (β glycine)
	**Cold Diffuse ISM**	40	3.2×10^{-6}	**9.7×10^{5}**	9.6×10^{5}	3×10^{7}
	**Dense ISM**	10	1.6×10^{-7}	**1.6×10^{7}**	1.7×10^{7}	-------

[1] M. H. Moore et al. 2001 AcSpA, 57, 843

The solar system

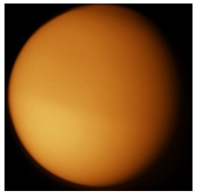
AU



AU

1 AU ≈ 150 000 km

Solar system objects

	Location	T (K)	Depth (cm)	Radiation dose rate (eV yr^{-1})	Glycine half-life (yr): This work 2 keV electrons	Glycine half-life (yr): Gerakines et al. 0,8 MeV protons	Glycine half-life (yr): Pilling et al. 2 keV electrons
	**Scatterd Disk 85 AU[1]**	40	10^{-4}	1.0×10^{-6}	**3.1×10^{6}**	3.1×10^{6}	---------
			10^{-2}	1.0×10^{-7}	**3.1×10^{7}**	----------	8.3×10^{8}
			1	7.7×10^{-9}	**4.0×10^{8}**	4.0×10^{8}	----------
	**Titan[2] 9 AU**	90	------	4.2×10^{-10}	**7×10^{9}**	-------	2.1×10^{11}

[1] Radiation dose rate from G. Strazzula et al., 2003, CRPhy, 4, 791
[2] Radiation dose rate from C. Sagan & W. R. Thompson, 1984, Icarus, 59, 133

Conclusions

- The effect of keV electron irradiation is similar to that of MeV protons for samples of thickness below the penetration depth of electrons. With this caveat **irradiation with keV electrons is a good means to simulate the effects of cosmic rays.**

- Decarboxylation is found to be the main primary mechanism for the destruction of glycine. The IR spectra of the radiolysis residues suggest the formation of polypeptides.

- With the lifetimes estimated from our measurements **there is a slim chance, but not a high probability that hypothetical interstellar glycine might have survived the passage from the pre-solar dense cloud to the present day solar sytem.**